

## REMARKS

### Rejection of Claims and Traversal Thereof

In the April 1, 2005 Office Action, the Office maintained the rejection of claims 1-17 under 35 U.S.C. §103(a) as being unpatentable over XP-002161407 (Rogowin S. A.). Applicants traverse such a rejection.

To establish a *prima facie* case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the reference itself or in the knowledge generally available to one skilled in the art, to modify the reference. Second, there must be a reasonable expectation of success. Finally, the prior art reference must teach or suggest all the claim limitations. Clearly, the Rogowin reference does not meet this standard.

As stated in applicants' December 28, 2004 response, Rogowin teaches that dry cellulose should be dissolved in water, with a calcium cation so that the carboxyl groups can be blocked. Thus, the first criteria would be satisfied if the reference provides some suggestion or motivation to avoid blocking the carboxyl groups with calcium, and instead, reduce the number of carboxyl groups. This motivation to modify the reference is very difficult to find in light of the results set forth in Table 33 of Rogowin and recreated below for ease of discussion.

Cellulose	Content of COOH-groups of the cellulose [%]	Decrease of the polymerization degree after heating based on the primary polymerization degree [%]
Beech tree pulp I	0.004	24.8
Beech tree pulp II	0.046	4.9
Pine tree pulp I	0.004	28.3
Pine tree pulp II	0.1	4.8

The test results set forth in Table 33 of Rogowin do not show that reducing the carboxyl groups provides any benefits or is an acceptable alternative. Instead, the results show that a cellulose sample with a reduced number of carboxyl groups (0.004 %) has a 25% reduction in polymerization. However, a cellulose sample with an increased number of carboxyl groups (0.046% or 0.1%) but blocked with calcium shows only a 4% reduction in polymerization. Thus

one skilled in the art would certainly understand that blocking the carboxyl groups is far more effective than having a lower number of carboxyl groups. What is the motivation put forth in the cited reference to lower the carboxyl count when in fact the results show that a cellulose with a lower carboxyl count exhibited reduced polymerization when compared to blocking the carboxyl groups with a calcium cation. Why would anyone even consider reducing the content number of carboxyl groups in the cellulose when the results show a large reduction in polymerization and **in the production of fibers---it is all about polymerization**. Clearly, the Rogowin reference does not meet the first requirement for establishing obviousness.

The second criterion that must be met includes some reasonable expectation of success when reducing the number of carboxyl groups, instead of blocking the carboxyl groups with calcium. Again, the results in Table 33 are not very promising because when the number of carboxyl groups is low (0.004%) there is a large reduction in polymerization. Certainly, polymerization is important, and as such, applicants doubt that one skilled in the art reading this reference would be willing to give up polymerization by reducing carboxyl groups.

Notably, Rogowin further discusses another problem with bleached cellulose, that being the formation of aldehydes, in addition to that of carboxyl groups, and these aldehyde groups have an important influence with respect to alkaline resistance and thermo resistance of the cellulose. Rogowin states that as the number of aldehyde groups increases, the resistance of cellulose against alkalines is reduced and the cellulose will be more intensively decomposed by the treatment with alkalines. Further, these aldehyde groups effect the discoloration of cellulose at higher temperatures. With these negative effects due to the aldehydes, one would be very concerned about introducing the cellulose into a strong alkaline solution. Instead, Rogowin teaches that the introduction of cellulose into water (with a pH of about 7) seems to address the problems of both the carboxyl groups and aldehyde groups. Specifically, the calcium in the water binds with the carboxyl groups, thereby blocking the carboxyl groups and also the water with a neutral pH does not decompose the material.

Interestingly, applicants do the exact opposite of that taught in Rogowin, they reduce the number of carboxyl groups and dissolve the cellulose in a strong alkaline solution. Clearly, the Rogowin reference provides no expectation of success when going in the direction of applicants' claimed invention. However, the Office contends that:

"Although Rogowin teaches that calcium blocking of carboxyl groups can decrease the amount of depolymerization, it does not eliminate the depolymerization completely. Elimination of carboxyl groups in the first place would achieve results at least as good as calcium blocking, if not better. Furthermore, elimination of carboxyl groups in the base material would eliminate the need for calcium blocking, which may not be feasible for all process." (emphasis added)

This statement by the Office is speculative at best because after a thorough review of Rogowin there is no statement made in the reference to reduce the carboxyl groups and with the expectation of any positive results. Instead, Rogowin discusses that an unbleached viscose (500-550 elementary elements) and bleached viscose (300-370 elements) both showed a yellowing during the longer drying period. Consequently, Rogowin comes to the conclusion, in the last paragraph of the reference, that the carboxyl groups have to be blocked by stating that "to obtain an increase of the light resistance and thermostability of the fibres, the carboxyl groups have to be blocked in the starting pulp or the hydrated pulp." Thus, Rogowin states that the carboxyl groups have to be blocked in the starting material which is in direct conflict with the contention of the Office that states "elimination of carboxyl groups in the base material would eliminate the need for calcium blocking, which may not be feasible for all process." Accordingly, if Rogowin states that calcium blocking is essential, where is there any motivation to bypass this blocking and instead reduce the number of carboxyl groups, as proposed by the Office? Clearly, there is none. In fact, this statement by Rogowin regarding the importance of calcium blocking in combination with the aldehyde discussion in the first section of the reference, relating to the detrimental effects of aldehyde groups especially in the presence of alkaline, provides evidence that the reference teaches away from going in the direction of applicants' claimed invention.

According to the Office, because Rogowin teaches that bleached cellulose exhibits discoloration and decomposition at high temperatures due to the presence of carboxyl groups, that this problem is present regardless what type of bleached cellulose is used or whether a particular solvent is possibly decomposed with the cellulose. However, this contention is not supported by the reference but merely by the Office's speculation. Rogowin recognizes that carboxyl groups and aldehyde groups are problematic and to rectify the problems, the carboxyl groups are blocked and an alkaline solution is avoided to overcome the problems related to the aldehyde groups.

As stated above, applicants have gone in the opposite direction from the teachings of Rogowin. Firstly, applicants dissolve the base material in a highly alkali environment, this is in spite of the

statement in Rogowin that cellulose is decomposed by the treatment of alkalines and that aldehydes effect discoloration of cellulose. Clearly, the lyocell process is so different from that of the viscose process, discussed in this 1960 Rogowin reference, that treatment of cellulose in the highly alkali environment of NMMO does not have a deleterious effect on the lyocell fiber. NMMO is a relatively strong oxidizing agent and used as an oxidizing agent in organic synthesis. Interestingly, NMMO oxidizes reducing ends in cellulose chains to aldehydes or carboxylic acids but also generates new keto structures along the chain by random oxidation of hydroxyl groups. Thus, by the mere process of mixing the NMMO with the cellulose, there is an increase in the production of carbonyl groups. Notably, an increase in aldehydes, is something that Rogowin is attempting to avoid by not contacting cellulose with a strong alkaline.

According to the Office, one skilled in the art would not consider there to be any difference between lyocell and viscose. Applicants vigorously contest this conclusion. Firstly, what needs to be corrected is that Colom et al., as provided on December 28, 2004, expressly states that the viscose fibers experience complete dissolution at high caustic concentration while for lyocell there is no dissolution. This reference from 2002 discusses facts that applicants discovered when they invented the presently claimed invention. Of course, this would not be known from the Rogowin reference because Lyocell was not even thought of in 1960 and Rogowin only discusses viscose. One skilled in the art, at the time this present invention was discovered, already knew that there were major differences between the viscose process and product and the lyocell process and product, even though they both use cellulose as starting material. Thus, one skilled in the art, at the time of filing of the present invention, would not look to the Rogowin reference for any guidance relating to the lyocell product or process of making same.

For example, in the table, recreated below, the differences between the different fibers are very evident.

*Journal of Applied Polymer Science, Vol. 35, 1987-2000 (1988)*

**The Fibrillar Structure of Cellulosic  
Man-Made Fibers Spun from Different  
Solvent Systems\***

**TABLE 1**  
Summary of the Fine Structural Data of All Investigated Fiber Samples

Fiber	TEM, length of the platelets (nm)	SAXS, long period (nm)	WAXD	
			Crystallinity (%)	Orientation factor fr
NMMO 1	14.4	18.7	54.8	0.60
NMMO 2	16.0	22.0	59.5	0.80
Carbamate 1	—	17.9	50.6	0.67
Carbamate 2	12.3	16.6	50.1	0.71
DMAc/LiCl 1	12.9	18.2	31.3	0.28
DMAc/LiCl 2	13.0	—	31.0	0.26
DMAc/LiCl 3	16.5	17.9	33.1	0.67
Modal	13.2	17.2	47.0	0.53
Polynosic	13.9	17.4	48.3	0.54
Viscose 1	10.0	14.3	33.0	0.36
Viscose 2	11.0	14.3	34.7	0.39








The data shows that lyocell has a much higher crystallinity percentage and the orientation of the fibers is more ordered than that of viscose. Furthermore, the length of the lyocell fiber is longer than that of the viscose. These results indicate that the products are not considered similar.

Likewise, this is shown and discussed in Woodings, submitted on December 28, 2004, where the specifics of the different characteristics are set forth in Table 1, recreated below.

Viscose
Lyocell

*Development of advanced cellulosic fibres: C. R. Woodings*

**Table 1** The properties of selected commercial rayon fibres

Property	Cuprammonium	Regular rayon	Improved rayon	Modal	Polynosic	"Y"-shaped rayon <sup>a</sup>	Solvent-spun rayon <sup>b</sup>
Fibre cross-section							
Dry tenacity (cN/tex)	15-20	20-24	24-30	34-36	40-45	18-22	40-44
Extensibility at break % (dry)	7-23	30-35	20-25	13-15	8-12	17-22	14-16
Wet tenacity (cN/tex)	9-12	10-15	12-16	19-21	30-40	9-12	34-38
Extensibility at break % (wet)	16-43	25-30	25-35	13-15	10-15	23-30	16-18
Water imbibition (%)	100	90-100	90-100	75-80	55-70	100-110	65-70
Cellulose D.P.	450-550	250-350	250-350	300-500	550-700	250-350	550-600
Initial wet modulus (@ 5%)	30-50	40-50	40-50	100-120	140-180	35-45	250-270

<sup>a</sup>The "Y"-shaped rayon data are based on Courtaulds' Galaxy fibre  
<sup>b</sup>The solvent-spun rayon data are based on Courtaulds' Tenax fibre

Clearly, the tenacity of lyocell compared to viscose is very different, whether in a wet or dry mode, and clearly, lyocell exhibits much higher strength in both wet and dry mode. The difference in the initial wet modulus is very significant because it is an indication of the strength of the fibers and the degree of tenacity required to produce an elongation of 5% when the specimen is completely wet. Additionally, the lyocell is a much stronger fiber because of the

required stress to stretch the fiber. The cross-sections of the fibers are also different wherein the viscose is serrated and the lyocell is circular.

Further, Woodings states that

The lyocell fibres now being introduced have the capability to halt the overall decline in manmade cellulosic fibres' share of the world market. In clothing textiles, Courtaulds' Tencel™ had early successes in market sectors which were previously closed to the other manmade cellulosic fibres. The combination of the unique fibre properties with novel fabric and garment finishing techniques yielded highly desirable garment aesthetics. These aesthetics have proved attractive in garments as diverse as denim and underwear.

In non-woven fabrics, lyocell's inherent strength and 'bondability' have led to a variety of new applications which were not possible with viscose rayon. In hydroentanglement, one of the fastest growing sectors of the non-woven industry, the use of Courtaulds' lyocell is now showing several advantages over other cellulosic fibres. Compared with viscose or cotton, it allows the manufacture of a wider range of basis weights, with higher strengths, better appearance and improved dry and wet textures. At high bonding pressures, it has enabled the production of non-woven fabrics which are stronger than the same weight of woven cotton. When fibrillated by refining or very-high-pressure hydroentanglement, the microfibrils generated may be used in leather- or suede-like materials, efficient filters, or even durable papers.

unique fiber properties

Comparison with Viscose

This unique fiber orientation of lyocell can be shown below:

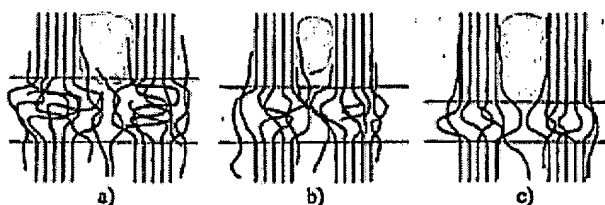


FIGURE 5. Accessible regions in structures of different kinds of regenerated cellulosic fibers: (a) viscose fibers, (b) modal fibers, (c) lyocell fibers [14].

14. Kreze, T., Sorption Characteristics of the Conventional and Alternative Regenerated Cellulose Fibers, Doctoral thesis, University of Maribor, 1999.

Thus, it is very evident that one skilled in the art, at the time of filling the present application, would know that the difference between viscose and lyocell is so significant that one would not even consider Rogowin as relating to the production of lyocell.

Lastly, the cited reference does not disclose each and every element of applicants' claimed invention. Where in the Rogowin reference is there any suggestion for using a cellulose material with a reduced number of carboxyl groups in NMMO? Unmistakably, there is no mention of taking such cellulose and dissolving same in NMMO in the Rogowin reference.

However, it is the Office's contention, of course with the help of applicants' disclosure, that one skilled in the art would read the Rogowin reference and immediately make a correlation from the production of viscose to that of lyocell. Of course, it is interesting that the Rogowin reference was published in 1960 and until the year 1999 no one skilled in the art made this connection until applicants provided the necessary blueprint to the Office.

Applicants argue that this rejection amounts to the application of an "obvious to try" standard which is known to be an improper standard for a §103 rejection. The Office contends that the Rogowin reference discusses reducing the number of carboxyl groups and there is sufficient teaching or suggestion to make the presently claimed invention obvious. However, applicants have reviewed the Rogowin reference and nowhere in this document is there any expressed statement that states that there should be a reduction in carboxyl groups. Instead, the reference only discusses blocking the carboxyl groups. Blocking and eliminating are two completely different actions. The translation states "carboxyl groups decrease thermostability of the cellulose but then immediately describes the need for blocking the carboxyl groups.

Further, this simple statement regarding the problems related to carboxyl groups in viscose material does not provide any guidance regarding the dissolving of cellulose in NMMO especially in light of the unpredictability of the additional oxidative reactions when using NMMO to dissolve cellulose. This very issue was recently addressed by the Board of Patent Appeals and Interferences in *Ex parte Goldgaber*, 41 USPQ2d 1172 (B.P.A.I. 1996) (quoting *In re Eli Lilly and Co.*, 14 USPQ2d 1741, 1743 (Fed. Cir. 1990)) and the Board stated that "an 'obvious-to-try' situation exists when a general disclosure may pique the scientist's curiosity, such that further investigation might be done as a result of the disclosure, but the disclosure itself does not contain

a sufficient teaching of how to obtain the desired result, or that the claimed result would be obtained if certain directions were pursued." (emphasis added).

Applicants contend that a general statement in Rogowin about blocking the content of carboxyl groups in viscose without any additional guidance is not sufficient to meet the Office's burden of establishing a *prima facie* case of obviousness. The speculation by the Office amounts to an "obvious to try" rejection and using the "obvious to try" test would often deny patent protection to inventions growing out of well-planned research which is, of course, guided into those areas in which success is deemed most likely. These are, perhaps, the obvious areas to try. But resulting inventions are not necessarily obvious. Serendipity is not a prerequisite to patentability. *In re Lindell*, 155 USPQ 521, 523 (C.C.P.A. 1967).

In light of the above discussion and the fact that (1) there is no motivation, suggestion or teaching to modify the reference; (2) there is no expectation of success by modifying the process in the reference and (3) each and every recited limitation of applicants' claimed invention is not disclosed or suggested in the cited reference, it is clear that the cited reference fails to establish a *prima facie* case of obviousness of applicants' claimed invention. Accordingly, applicants request the withdrawal of this rejection.

### Conclusion

Applicants have satisfied the requirements for patentability. All pending claims are free of the art and fully comply with the requirements of 35 U.S.C. §112. It therefore is requested that Examiner Osele reconsider the patentability of all pending claims in light of the current amendment, and withdraw all rejections, thereby placing the application in condition for allowance. Notice of the same is earnestly solicited. In the event that any issues remain, Examiner Osele is requested to contact the undersigned attorney at (919) 419-9350 to resolve same.

Respectfully submitted,



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# The Fibrillar Structure of Cellulosic Man-Made Fibers Spun from Different Solvent Systems\*

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## Synopsis

The development of new methods of spinning cellulosic fibers requires a better understanding of their fibrillar structure in order to explain their special physical properties. By means of transmission electron microscopy (TEM), light microscopy (LM), small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD) it is shown that six different kinds of regenerated cellulosic fibers consist of uniform elementary fibrils composed of cellulose-II crystals. Systematic distinctions between these fiber types are found with regard to the aggregation of the elementary fibrils to nonswelling bundles or clusters. The clusters differ from each other in diameter, length, and frequency of occurrence.

## INTRODUCTION

Frey-Wyssling was the first who suggested that the microfibrils of natural occurring cellulose I were the product of fasciation of crystalline smaller threads, to which he gave the name of "elementary fibrils." They should have the shape of long ribbonlike strings with a cross section of approximately  $3 \times 7$  nm. The strings were held together by amorphous material to form the whole microfibril.<sup>1</sup> Preston, however, concluded that these results, found by means of TEM, are artifacts with respect to the existence of elementary fibrils.<sup>2</sup> Sullivan observed that the diameters of the so-called elementary fibrils are dependent on the time the material was subjected to the ultrasonic treatment.<sup>3</sup> Heyn was the first to apply the preparation technique of negative staining to the electron-microscopic study of the fibrillar structure of natural cellulose fibers.<sup>4</sup> Unlike the metal shadowing, staining is carried out in the uncollapsed, water-swollen state, in which the staining solution penetrates between the fibrils and is deposited there upon drying. Therefore, conglomeration and collapsing to artifacts during drying may be largely prevented. Heyn detected beaded appearing elementary fibrils with a periodic change of crystallinity. The crystals were clearly visible, because only the amorphous portions take up the stain, the crystalline portions remaining unstained. Preston's criticism of this method is based on the assumption that the fibrils have a circular cross-section; in fact, it is rectangular.

\*Paper presented on occasion of the International Dissolving Pulps Conference, March 24–27, 1987, in Geneva, Switzerland.

Apart from natural cellulose fibers regenerated cellulosic fibers were studied using hydrolysis, ultrasonic treatment, and metal shadowing by Dlugosz and Michie,<sup>5</sup> Mühlethaler,<sup>6</sup> Takai et al.,<sup>7</sup> Ribi,<sup>8</sup> and Mukherjee et al.<sup>9</sup> Schurz and John used iodination according to Hess and detected in fibrils of Fortisan a periodicity in the order of the long period.<sup>10</sup> Manley<sup>11</sup> again used the negative staining technique. In Fortisan he detected thin parallel filaments about 3 nm in width, which looked like beadchains similar to the fibrils found by Heyn.<sup>11</sup> Lenz et al. found in hydrolyzed viscose fibers chains of platelets, the dimensions of which were consistent with the wide- and small-angle X-ray data.<sup>12</sup> Nevertheless, the existence of elementary fibrils is still controversial today.

In contrast to natural cellulose fibers, there is till now no evidence for the existence of microfibrils in man-made cellulosic fibers.

## EXPERIMENTAL

### Fiber Samples

NMMOs 1 and 2 are fibers spun from a solution of cellulose in *N*-methylmorpholineoxidehydrate (Akzona). DMAc/LiCl 1, 2, and 3 are fibers spun from a solution of cellulose in dimethylacetamide/lithiumchloride (laboratory). Carbamates 1 and 2 are fibers spun from a solution of cellulose carbamate in sodium lye (Neste OY). Modal is a high wet modulus fiber (Lenzing AG). Polynosic is polynosic fiber (Toyobo). Viscose 1 is a viscose fiber (Lenzing AG), and viscose 2 is a high tenacity viscose fiber (Lenzing AG).

### Preparation of Samples

For X-ray examinations the fiber samples were hydrolyzed 24 h at 60°C in 1*N* HCl, washed and dried. The weight loss varied from 2.5% (Polynosic) to 7% (modal). After this treatment a level-off DP of 130 was determined. For transmission electron microscopy the samples were hydrolyzed 48 h and subsequently ultrasonified for 15–60 min.

### Determination of the Long Period by Means of SAXS

The specimens were subjected to X-ray examination in their original fibrous form. The X-ray scattering curves were obtained by means of a Kratky camera equipped with a slitfocus. The width of the entry slit was 60 μm, the width of the counting tube slit 150 μm. An X-ray tube with Cu target and Ni filter was run with a commercial X-ray unit. The long period could be obtained clearly from the line profiles at 2θ of maximum peak.

Bragg's equation was used for the calculation of the long period

$$2d \sin \theta = n \cdot \lambda \quad (1)$$

where *d* is the period of identity of the electron density fluctuation along the fiber axis, *n* is an integer, *θ* is half the scattering angle, and *λ* is the wavelength (Cu K<sub>α</sub>: 0.15418 nm).

### Determination of the Lateral Period of Identity by Means of SAXS

The same technique was used as described above with the difference that the fiber specimen was arranged in the camera horizontally instead of vertically. For the X-ray examination of the fibers in the swollen state the specimen containing the glass tube was connected by a flexible pipe with a

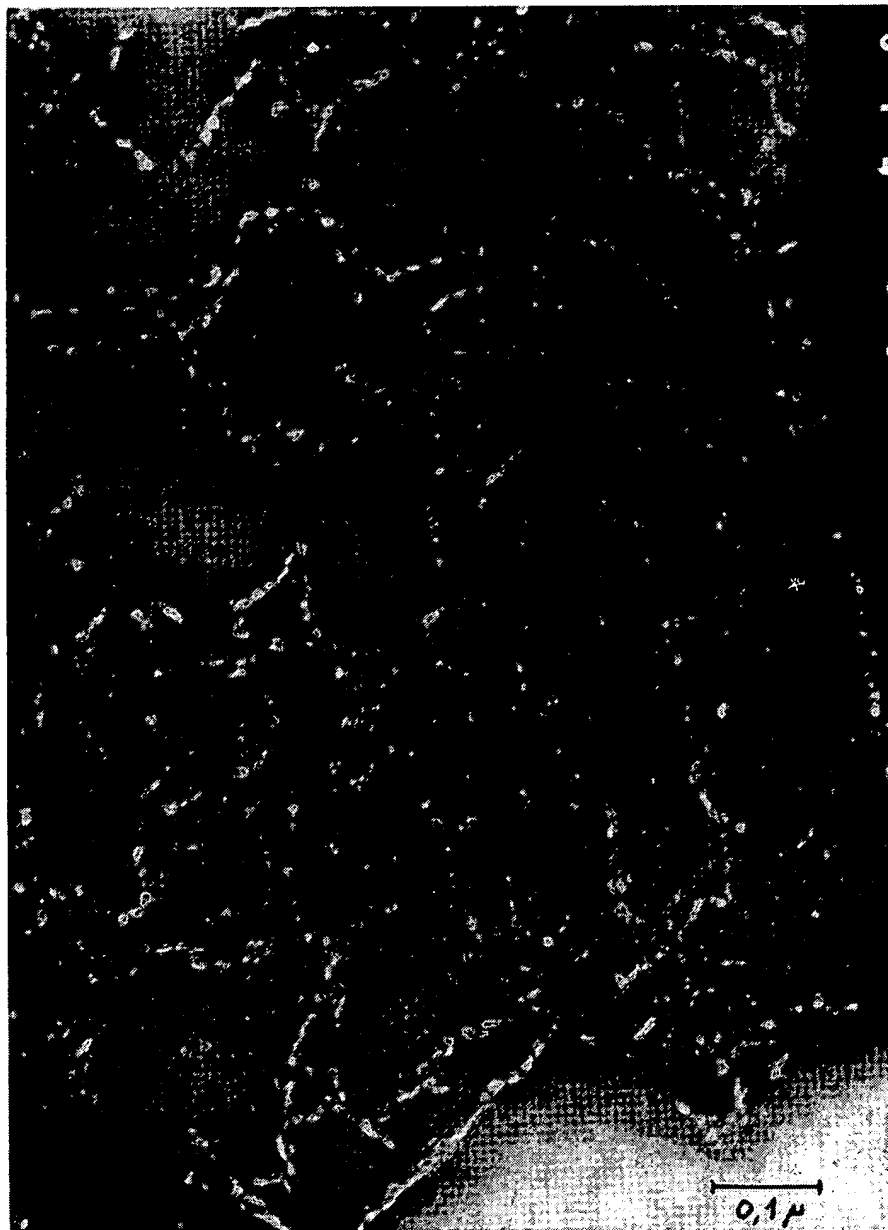


Fig. 1. Transmission electron micrograph of a hydrolyzed, disintegrated modal-fiber (magnification  $204,000\times$ , hydrolyzing time 50 h, ultrasonic treatment 15 min).



Fig. 2. Transmission electron micrograph of a hydrolyzed, disintegrated fiber, spun from a solution of cellulose in dimethylacetamide/LiCl (magnification  $204,000\times$ , hydrolyzing time 60 h, ultrasonic treatment 20 min).

water reservoir. In the equation  $d$  means the period of identity normal to the fiber axis.

#### **Determination of the Degree of Crystallinity and the Orientation Factor by Means of WAXD**

The degree of crystallinity was determined by means of planimetry of the equatorial wide-angle X-ray diffractograms. The curve for the elimination of the background was drawn visually. From the azimuthal intensity distribution of the well-resolved wide-angle X-ray reflection lines  $10\bar{1}$  and  $101$ , the orientation factor was calculated according to Kratky.<sup>15</sup>

#### **Determination of the Size of Crystallites and Clusters by Means of TEM**

After a hydrolyzing time of 48 h in 1N HCl at 60°C the fibers were found to be destroyed. In some cases hydrolyzing had to be prolonged for 100 h. Afterward the fibril suspension was further disintegrated by means of a Bronson Sonifier 830 at 150 W and 20 Hz. The applied times of hydrolyzing and sonifying did not change the dimensions of the crystallites. The material was prepared for TEM according to the method of negative staining with phosphotungstic acid. It is assumed, that the amorphous portions take up the stain, whereas the crystalline portions remain unstained (Figs. 1 and 2). On each electron micrograph we measured the maximum length, width, and thickness of each well visible oval shaped platelet. Each given value is the average of 80 measurements. Moreover, we measured both length and diameter of each bundle of elementary fibrils.

#### **Determination of the Degree of Swelling by Means of LM**

The diameter of the weakly hydrolyzed fibers was measured by means of a measuring ocular as well in the dry as in the wet state, i.e., immersed in water. Each value is the average of 20 measurements.

### **RESULTS AND DISCUSSION**

The electron micrographs of the hydrolyzed fibers show strings of platelets, which occur either isolated (Fig. 1) or aggregated to bundles (Fig. 2). If these strings are identical with elementary fibrils, the platelets must be cellulose-II crystals. In order to identify these morphological units, we measured the long periods of the corresponding weakly hydrolyzed fiber samples being aware of the fact that acidic hydrolysis increases the original crystal size.

In Table I the following data are put together: the average length of the platelets, the long period, the degree of crystallinity, and the crystalline orientation factor. As is to be seen, the long periods are 30–40% larger than the lengths of the platelets. This is due to the fact that the long period covers the length of a whole period of electron density fluctuation including the less ordered interspace between two crystallites. From the rather constant ratio between the length of the platelets and the long period we conclude that the platelets are in fact cellulose-II crystals. If this is true, the beaded chains on the electron micrographs must be elementary fibrils.

TABLE I  
Summary of the Fine Structural Data of All Investigated Fiber Samples

Fiber	TEM, length of the platelets (nm)	SAXS, long period (nm)	WAXD	
			Crystallinity (%)	Orientation factor fr
NMMO 1	14.4	18.7	54.8	0.60
NMMO 2	16.0	22.0	59.5	0.80
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DMAc/LiCl 1	12.9	18.2	31.3	0.28
DMAc/LiCl 2	13.0	—	31.0	0.26
DMAc/LiCl 3	16.5	17.9	33.1	0.67
Modal	13.2	17.2	47.0	0.53
Polynosic	13.9	17.4	48.3	0.54
Viscose 1	10.0	14.3	33.0	0.36
Viscose 2	11.0	14.3	34.7	0.39

If cellulosic fibers consist of regularly shaped fibrils, the latter must be detectable also by measuring the equatorial SAXS curve, because their existence would implicate electron density fluctuations normal to the fiber axis. In 1953 Hermans and co-workers already discovered in the equatorial SAXS curves of certain regenerated cellulose fibers a small inflection or bulge, caused by a superimposed interference maximum, which he supposed to be an indication of the presence of uniform, lamella-like particles packed in a regular manner.<sup>13</sup> From the scattering angle, at which the inflection appears, he calculated a lateral period of identity using eq. (1). He found 4.5–5.5 nm for dry fibers and 7.0–8.5 nm for water-swollen fibers. Heyn made similar observations.<sup>14</sup>

Because the monoaxially oriented fibers are arranged parallel to the streak-like focus of the Kratky camera; the effect of the Lorentz factor of the lamella length and the smearing of the gap neutralize each other. For this reason the Lorentz factor must not be eliminated from the scattering curves. That means according to Kratky that the position of the superimposed interference maximum of the equatorial SAXS curve is a useful measure for the upper limit of the width of a lamella.<sup>15</sup> So the occurrence of an interference maximum in the equatorial SAXS curve is an indication that the scattering particles must be lamella-shaped bodies ordered parallel to each other. This picture would be consistent with the existence of ribbonlike elementary fibrils.

Following up these considerations, we measured the equatorial SAXS curves of the fiber samples in the dry and water-swollen state. Two examples are shown in Figures 3 and 4. In conformity with Hermans' results the dry fibers show a weak inflection at a period of identity of 6–7 nm, whereas the wet fibers show a strong interference maximum at a lateral period between 9 and 18 nm. In Table II, columns 1 and 2, the results are listed.

The question arises why the inflections in the wet state are more distinct and correspond to a larger lateral period. In this respect one has to realize that the basic equatorial SAXS curve of a dry cellulose fiber is caused by pores of colloidal dimensions.<sup>16</sup> Through swelling of the fibers in water, these voids will be filled, causing a sharper appearance of the interference maxi-

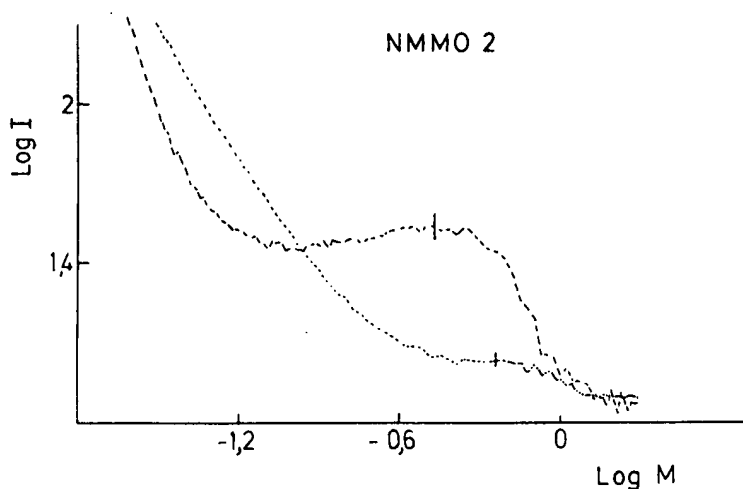


Fig. 3. Equatorial SAXS curve of a fiber, spun from a solution of cellulose in *N*-methylmorpholineoxidehydrate: (···) dry state; (---) wet state.  $M$  = scattering angle as distance from the center of the primary beam;  $I$  = X-ray scattering intensity.

mum. In addition, the particles will be separated from each other by swollen less-ordered cellulose, giving rise to a larger period of identity normal to the fiber axis.

Columns 4 and 5 of Table II show width and thickness of the cellulose-II crystals measured by means of TEM. The average thickness of the crystals of 2.5–3 nm amounts approximately to 40% of the lateral period in the dry state in the range of 6.0–7.0 nm. As the crystals are covered with less-ordered cellulose, one has to expect a difference between the thickness of the crystals and the lateral period in the order of the crystallinity. The latter ranges between 30 and 60% according to Table I, column 3.

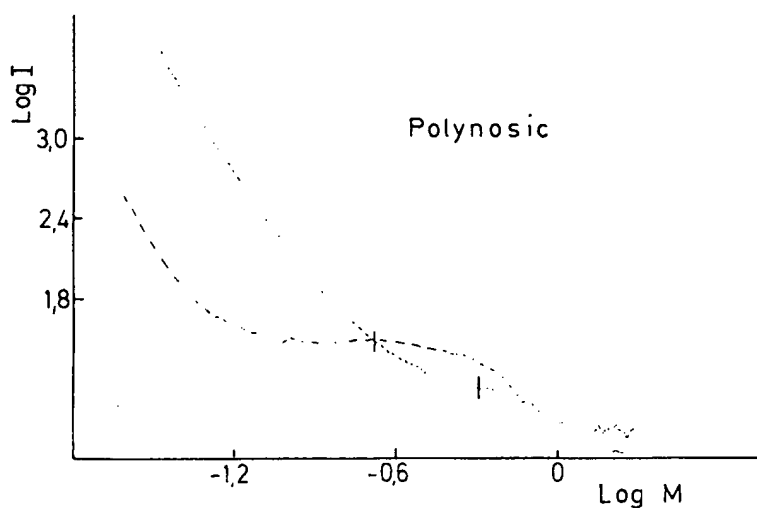


Fig. 4. Equatorial SAXS curve of a polynosic fiber.



TABLE II  
Internal and Macroscopic Swelling of the Fiber Samples

Fiber	SAXS, lateral period			TEM: Width Thickness of crystals		LM, macroscopic swelling (degree)	Cluster fraction
	Dry (nm)	Wet (nm)	Increase (degree)	(nm)	(nm)		
NMMO 1	6.0	12.4	2.06	7.1	2.5	1.66	0.38
NMMO 2	6.9	9.1	1.32	6.2	2.6	1.23	0.28
Carbamate 1	6.7	12.9	1.93	—	—	—	—
Carbamate 2	6.1	16.6	2.70	8.8	2.6	—	—
DMAc/LiCl 1	6.5	18.2	2.78	7.9	2.6	1.27	0.85
Modal 1	7.0	13.8	1.97	8.7	3.1	1.13	0.87
Polynosic	6.4	15.5	2.44	7.6	2.5	1.34	0.76
Viscose 1	6.5	18.5	2.86	6.3	2.4	1.31	0.83
Viscose 2	6.6	18.4	2.79	5.1	1.9	1.23	0.87

In contrast to the dry state the lateral periods in the swollen state differ strongly from each other. The increase of the lateral period by water swelling varies between 30 and 180%. That means that the less-ordered cellulose between the crystals must take up different amounts of water. This conclusion will be supported by the fact that the increase of the lateral period by swelling correlates in inverse proportion with the crystalline orientation factor, as is shown in Figure 5.

In comparison with the internal degree of swelling, the macroscopic degree of swelling was also determined by light microscopical observation of the increase of the thickness of the in-water immersed fibers. The results are given in column 6 of Table II. Comparing the internal with the macroscopic degree of swelling, it becomes evident that the latter is much less than the former. That means that a certain portion of the fiber substance does not swell in water.

In so-called air-swollen cellulose, which is swollen and subsequently porously dried viscose fiber, Kratky found a portion of the material being present in the form of large, dense particles or clusters of cellulose crystals.<sup>17</sup> Assuming that in water-swollen fibers such nonswollen clusters may occur, too, the degree of the supposed cluster formation of the different fiber samples was calculated from the internal and macroscopic degree of swelling using the following equation given by Kratky and Miholic:<sup>17</sup>

$$f = (q - q') / (1 - q') \quad (2)$$

where  $f$  means the cluster fraction,  $q$  the macroscopic degree of swelling, and  $q'$  the internal degree of swelling. The portions of the assumed cluster fraction are listed in the last column of Table II. The values are astonishingly high.

The assumption of the existence of nonswelling bundles of elementary fibrils is supported by the transmission electron micrographs. They show such bundles, which obviously did not swell during hydrolysis, ultrasonic treatment, and staining even after very prolonged treatments.

Because a morphological observation is no proof, showing the existence of nonswelling clusters was tried by measuring the equatorial SAXS curves of

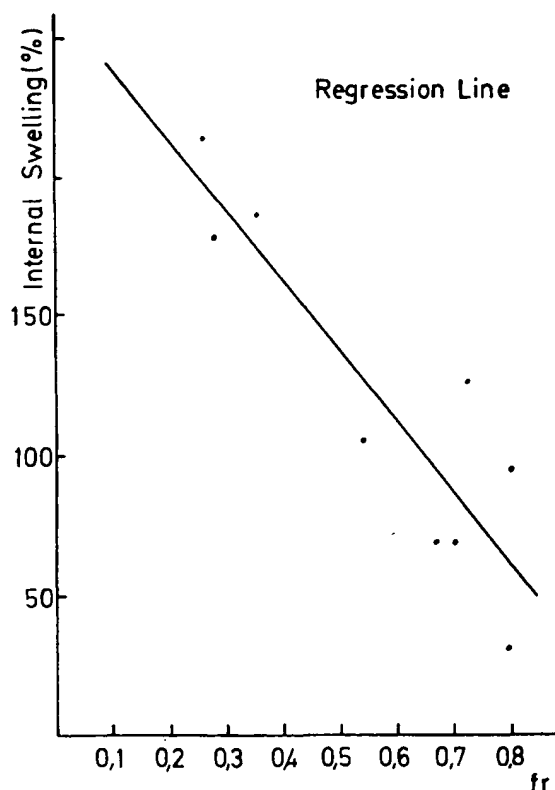


Fig. 5. Correlation between the internal swelling and the orientation factor (fr): coefficient of correlation  $-0.894$ ; statistical confidence 99.9%.

the weakly hydrolyzed water-swollen fibers at extremely small angles according to Guinier's theory of particle scattering. Infinitely diluted particles of colloidal dimensions give rise to an X-ray scattering curve, which in the Guinier plot, i.e., the logarithm of the scattering intensity vs. the square of the scattering angle, approaches with decreasing scattering angle to a straight line.<sup>18</sup> In a monoaxially oriented, monodisperse system the limiting slope of the Guinier curve is a function of the radius of gyration of the cross section of the scattering particles. Assuming a circular cross section of the elongated scattering particles, infinite length with respect to the wavelength, and parallel orientation, one can calculate the cluster diameter according to the following equations:<sup>19,20</sup>

$$Rq = 0.526 \cdot a \cdot \sqrt{\tan \alpha} \quad (3)$$

$$Rq^2 = r^2/2 \quad (4)$$

where  $Rq$  means the radius of gyration of the cross section,  $\alpha$  the slope of the curve of  $\log I$  vs  $M^2$ ,  $r$  the radius of the cylindrical particle,  $a$  the distance between sample and counting tube,  $I$  the scattering intensity, and  $M$  the scattering angle as distance from the center of the primary beam. If, however,

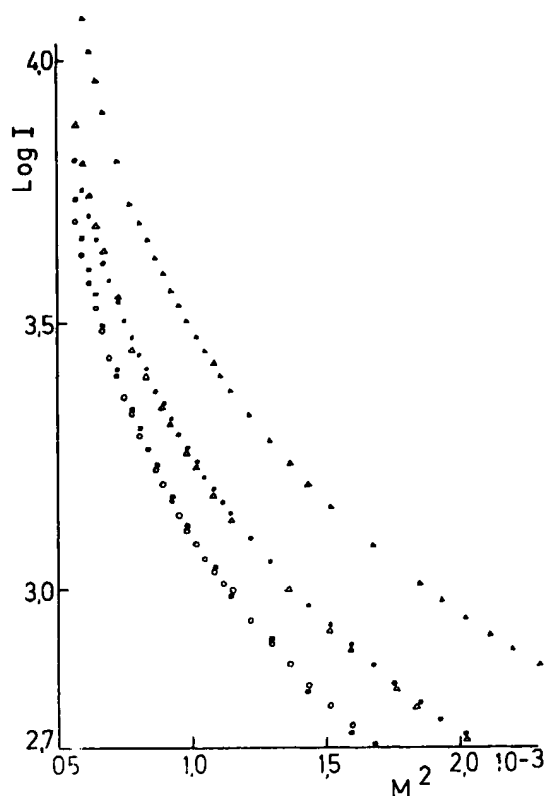


Fig. 6. Equatorial SAXS curves of different cellulosic fibers in Guinier plot in dry state: (●) NMMO 2; (○) modal 1; (△) viscose 1; (■) DMAc/LiCl 1; (▲) carbamat 1.

the Guinier plot has a curvature convex in relation to the ordinates, the particles do not scatter independently from each other, because of interference effects.

Figure 6 shows the Guinier plot of the fiber samples in the dry state. Obviously the inner part of the curves does not run out into a straight line approaching the scattering angle zero. This is due to the fact that the dry fiber is a densely packed system in which interparticle interference effects are dominant. Particle scattering occurs only in very porous fibers, such as air-swollen, viscose fibers<sup>17</sup> or porous polyacrylonitrile fibers.<sup>19</sup>

Figure 7 represents SAXS curves in the Guinier plot, which were obtained by exposing the immersed, swollen fibers to X-ray examination. Under these conditions the curves show straight-lined sections with distinct slopes. This curvature can be interpreted as the superposition of different Guinier scattering curves of a polydisperse system. Bearing in mind that the scattering of open pores in swollen fibers has to be neglected, this scattering must be due to dense particles of different diameter distributed in a matrix of water-swollen cellulose. Two kinds of fibers show a different curvature, as is seen in Figure 8, namely modal and carbamate fibers. Again these curves are convex in relation to the ordinates. Evidently in these fibers the clusters do not scatter independently from each other. However, these curves also run out into a straight

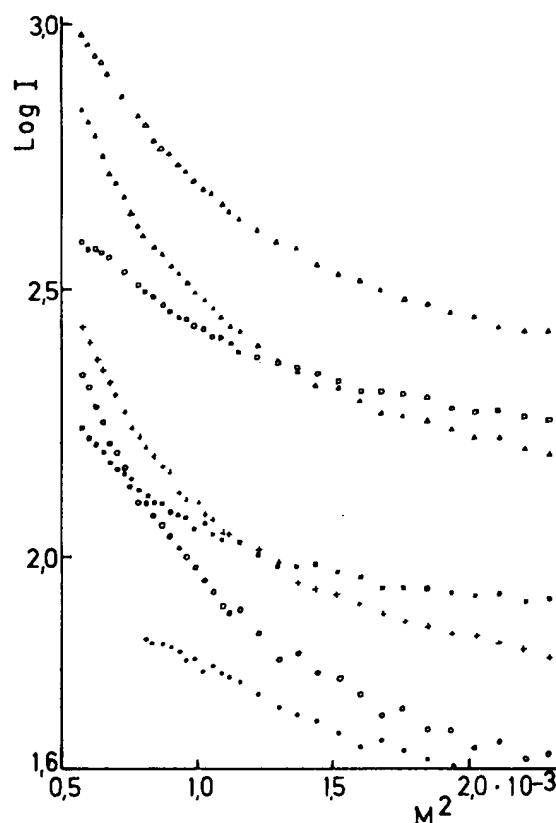


Fig. 7. Equatorial SAXS curves of different cellulosic fibers in a Guinier plot in a water-swollen state: (●) NMMO 1; (○) NMMO 2; (■) DMAc/LiCl 2; (□) DMAc/LiCl 1; (+) DMAc/LiCl 3; (Δ) viscose 1; (▲) modal 3.

line, which in the direction of increasing scattering angles turns into the interference maximum of the elementary fibrils.

An attempt was made to calculate the cluster diameters from the slopes of the straight-lined curve sections. As the measured curves are the result of a superposition of different scattering curves, corresponding to different cluster sizes, the latter would have to be separated before the evaluation. Regarding the short length of the straight-lined sections this would be problematic. Therefore, only the outmost curve sections having the lowest slope were evaluated assuming that this part of the SAXS curve is caused by only one particle size. As the sections are rather short, one has to bear in mind that the calculated values correspond to the lower limit of the cluster diameter.

Table III shows the cluster diameters, calculated from the straight-lined curve section, which has the lowest slope, using the eqs. (3) and (4). Comparing these values with the average diameters of the bundles of elementary fibrils, which were gained by evaluation of the TEM micrographs, a certain conformity can be noticed. At each sample the cluster diameter calculated from the SAXS curves lies within the variation of the average diameter of the bundles measured on the micrographs.

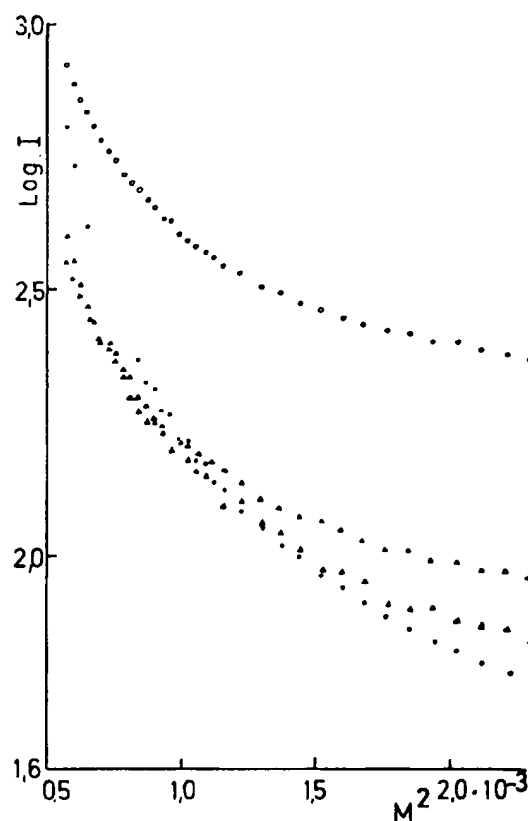


Fig. 8. Equatorial SAXS curves of different cellulosic fibers in a Guinier plot in a water-swollen state: (●) carbamat 1; (○) carbamat 2; (▲) modal 1; (Δ) modal 2.

TABLE III  
Dimensions of the Clusters by TEM and SAXS

Fiber	Cluster diameter			
	SAXS (nm)	TEM		Cluster length, TEM (nm)
		(nm)	(SD)	
NMMO 1	50.6	36.5	18.1	289
NMMO 2	51.7	47.0	—	243
Carbamate 2	32.3	54.0	—	> 400
DMAc/LiCl 1	28.6	40.7	17.6	> 400
DMAc/LiCl 2	28.2	40.7	17.6	> 400
DMAc/LiCl 3	37.7	44.6	22.1	> 400
Modal 1	33.7	39.4	18.1	184
Polynosic	51.5	35.9	—	188
Viscose 1	48.3	49.0	13.0	150
Viscose 2	30.8	43.2	17.4	144

In the fourth column of Table III the lengths of the clusters taken from the TEM micrographs are put together. Comparing these values, one notices great distinctions between the different fiber samples. In the cases of the DMAc/LiCl and carbamate fibers, the cluster lengths are larger than 400 nm, as at the other kinds of fibers the clusters are as short as 150–240 nm. Possibly the clusters of distinct fiber types are different stable against the ultrasonic treatment. Supposedly, one observes only fragments of the original clusters on the micrographs of the disintegrated fiber samples.

### CONCLUSION

The results show that all investigated kinds of fibers spun from different solvent systems consist of uniform elementary fibrils. In contrast to this result, there are systematic distinctions between the different fiber types regarding the aggregation of the elementary fibrils to nonswelling clusters.

Table II shows that fibers spun from a solution of cellulose in *N*-methylmorpholineoxide hydrate exhibit the lowest cluster fraction. Regarding Table III, it is remarkable that the cluster lengths harmonize within certain fiber types. Obviously the cluster length increases in the following order: normal viscose fibers, high wet modulus fibers, *N*-methylmorpholineoxide fibers, and fibers spun from a solution of cellulose in dimethylacetamide/lithiumchloride, respectively, from a solution of cellulose carbamate in sodium lye. It should be mentioned that the corresponding elongations at break decrease in the same sequence, if the fibers are oriented during their production to the maximum: normal viscose fibers 16–17%, high wet modulus fibers 11–14%, *N*-methylmorpholineoxide fibers 11%, and dimethylacetamide/lithiumchloride fibers 6–8%. Carbamate fibers make an exception with an elongation at break of 11–13%.

So it seems that the formation of very stable, long bundles of elementary fibrils reduces the elongation at break at a given orientation. This assumption is reasonable because the rupture of a fiber during stretching is the result of microstresses, which are more likely in the presence of rigid bodies being unable to comply with the external tension.

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